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THE FUGACITIES OF STEAM AND ACETYLENE AT HIGH PRESSURES*

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Introduction

Knowledges of the fugacities of gases are necessary for the considerations of the equilibrium at high pressures. The fugacity of steam at high temperatures and high pressures is especially interesting in connection with geochemisty and Holser[1] has calculated it from Kennedy's P-V-T data of steam[2]. In this paper, the fugacity of steam in the range of temperature from 380 to 460°C and that of pressure from 100 to 800 atm is calculated from the P-V-T data recently published by Kiyama, Kinoshita and Kitahara[3]. The results of the author are fairly well in accordance with the results of Holser at 400°C.

Now the reactions involving acetylene at high pressures are exceedingly important in chemical industry and considerations of equilibriums in such systems necessitate a knowledge of the fugacity of acetylene which has not yet been reported over the wide range of temperature and pressure.** In this paper the fugacity of acetylene in the range of temperature from 0 to 250°C and of pressure from 10 to 130 atm is also calculated from the P-V-T data of acetylene published by Kiyama, Ikegami and Inoue[4].

Methods

The fugacity coefficient $\nu_{T,P}$ is equal to the ratio of the fugacity f to the pressure P and the results of the calculations are expressed in this term,

$$\nu_{T,P}=f/P\,. \tag{1}$$

The change of fugacity coefficient with pressure is expressed by Eq. (2),

$$\ln \frac{\nu_{T,P}}{\nu_{T,P_0}}=\int_{P_0}^{P}\frac{1-Z}{P}dP\,, \tag{2}$$

where $Z=\dfrac{PV}{RT}$.

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* *This investigation has been done by H. Hiraoka, being in the postgraduate course, under direction of Prof. R. Kiyama.*

** The fugacity of acetylene at low temperatures has already been reported and used in the considerations of the solubility of acetylene. *cf. This Journal*, 24, 13 (1954), 25, 58 (1955)

1) W. T. Holser. *J. Phys. Chem.*, 58, 316 (1954)
2) G. C. Kennedy, *Am. J. Sci*, 248. 540 (1950)
3) R. Kiyama, H. Kinoshita and S. Kitahara, *This Journal*, 25. 21 (1955)
4) R. Kiyama, T. Ikegami and K. Inoue, *ibid.*, 21, 58(1951). *cf.* H. Teranishi, *ibid.*, 25, 25(1955)

The calculation of the fugacity of steam The change of fugacity coefficient with pressure is calculated graphically by Eq. (2) from the *P-V-T* data of steam of Kiyama *et al.*, which does not involve the data at lower pressures than 100 atm. Keyes, Smith and Gerry[5] reported the equation of state for steam,

$$P=\frac{4.5504\,T}{v-B} \quad , \tag{3}$$

where

$$B=B_0+B_0^2g_1(\tau)P\tau+B_0^4g_2(\tau)P^3\tau^3-B_0^{13}g_3(\tau)P^{12}\tau^{12} \quad ,$$

$$B_0=1.89-2641.62\times10^{80370\tau^2}\cdot\tau \quad ,$$

$$g_1(\tau)=82.546\tau-1.6246\times10^5\cdot\tau^2 \quad ,$$

$$g_2(\tau)=0.21828-1.2697\times10^5\cdot\tau^2 \quad ,$$

$$g_3(\tau)=3.635\times10^{-4}-6.768\times10^{64}\cdot\tau^{24} \quad ,$$

$$\tau=1/T \quad .$$

In Eq. (3) v is the volume expressed in cc occupied by 1 gram of steam and T is absolute temperature. The base values of the fugacity coefficient at 100 atm are calculated analytically from Eq. (4), which can be derived by substitution of the equation of state valid for this range into the thermodynamic equation,

$$\log \nu_{T,P}=\frac{18.02}{2.303RT}\left\{B_0P+\frac{(B_0P)^2g_1}{2T}+\frac{(B_0P)^4g_2}{4T^3}-\frac{(B_0P)^{13}g_3}{13T^{12}}\right\}. \tag{4}$$

The third and the fourth terms in the parenthesis of Eq. (4) may be negligible at high temperatures.

The calculation of the fugacity of acetylene The change of the fugacity coefficient of acetylene with pressure is calculated graphically from the *P-V-T* data of acetylene of Kiyama *et al.* which has the postulation that acetylene gas at 1 atm obeys the ideal gas law at each temperature. The correction for the deviation of acetylene at 1 atm from the ideal gas is done with the real molal volume of acetylene at 0°C and 1 atm=22.1656 ml and the thermal expansion coefficient of acetylene=0.00374.

The *P-V-T* data previously publisbed by Sameshima[6] and Rimarski,[7] which are valid at low pressures, cover the narrow range of temperature, so that the use of the approximate equation of fugacity is unavoidable in order to obtain the base

Equation for fugacity coefficient	ν at 10 atm	
	0 °C	25 °C
$\nu=\exp\left(\int_{P_0}^{P}\frac{1-z}{P}dp\right)$	0.9049	0.9233
$\nu\approx\frac{PV}{RT}$ [8]	0.9092	0.9291
$\nu\approx2-\frac{RT}{PV}$ [9]	0.9001	0.9237
$\nu\approx\frac{1}{2-\frac{PV}{RT}}$ [10]	0.9168	0.9338

5) F. G. Keyes, L. B. Smith and H. T. Gerry, *Proc. Am. Acad. Arts and Sci.*, 70, 317 (1936)

values at 10 atm in the range of temperature from 0 to 130°C. The approximate equation of fugacity coefficient is proposed in several different forms. In the above table the fugacity coefficients at 10 atm calculated from Sameshima's data are compared with the results obtained from these different approximate equations, where the value of $\frac{PV}{RT}$ at 10 atm is taken from Sameshima's data[6].

The above table shows that even at these low temperatures the error involved in these approximate values is small and at higher temperatures than 70°C all these approximate equations give the same values at 10 atm. By its simplicity and correct applicability as shown in the above table the first approximate equation, $\nu \approx \frac{PV}{RT}$, is used in the calculation of the base values at 10 atm and the fugacity coefficients at high pressures are calculated on these values.

Results

The fugacity coefficients of steam and acetylene calculated by the above process are shown in Tables 1 and 2 respectively. Fugacity is obtained by the multiplication of these values with pressure. The fugacity coefficients of steam at 400°C given in Table 1 show only slight deviation less than 1% from Holser's results. The values predicted from Newton's diagram based on the law of corresponding states show a few per cent deviations in both cases of steam and acetylene.

Table 1 The fugacity coefficients of steam

Press., atm \ Temp., °C	380	400	420	440	460
100	0.853	0.868	0.882	0.894	0.905
200	.706	.738	.772	.791	.812
300	.532	.597	.655	.690	.722
400	.422	.483	.546	.594	.633
500	.357	.409	.467	.516	.558
600	.313	.361	.413	.461	.499
700	.282	.325	.374	.418	.455
800	.259	.297	.345	.386	.421

6) J. Sameshima, *Bull. Chem. Soc. Japan*, 1, 41 (1926)
7) W. Rimarski and M. Konschak, *Autogene Metallbearbeitung*, 26, 129 (1933)
8) G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw Hill Book Co. 1924
9) *cf.* I. Prigogine and R. Defay, *Chemical Thermodynamics*, Longmans Green and Co. 1954
10) H. H. Elrod, *Ind. Eng. Chem.*, 47, 2199 (1955)
11) R. H. Newton, *Ind. Eng. Chem.*, 27, 302 (1935)

Table 2 The fugacity coefficients of acetylene

Temp., °C / Press., atm	0	10	20	30	40	50	60	70	80	90	100	125	150	175	200	225	250
10	0.898	0.912	0.926	0.938	0.949	0.959	0.968	0.975	0.980	0.982	0.985	0.987	0.990	0.992	0.994	0.994	0.996
20	.838	.832	.857	.878	.899	.916	.933	.946	.956	.961	.997	.972	.978	.982	.986	.987	.991
30		.753	.788	.818	.846	.870	.893	.912	.926	.935	.943	.953	.962	.969	.975	.978	.983
40			.660	.758	.792	.822	.850	.874	.892	.903	.914	.930	.942	.953	.961	.966	.973
50				.696	.738	.773	.806	.834	.855	.870	.883	.905	.921	.935	.945	.952	.961
60					.680	.723	.762	.793	.818	.836	.851	.879	.899	.916	.929	.938	.949
70					.617	.670	.717	.752	.780	.801	.819	.850	.878	.898	.913	.924	.937
80					.555	.616	.670	.711	.744	.768	.788	.826	.858	.881	.898	.911	.925
90						.570	.624	.671	.709	.736	.759	.803	.839	.865	.884	.899	.914
100						.527	.581	.633	.675	.705	.731	.781	.821	.850	.871	.887	.905
110						.491	.545	.598	.643	.677	.704	.760	.804	.835	.858	.876	.895
120						.461	.513	.567	.613	.649	.678	.739	.787	.821	.846	.865	.886
130						.436	.487	.539	.583	.623	.654	.719	.771	.807	.834	.855	.877

The author wishes to express his hearty thanks to Professor R. Kiyama for having initially suggested the study of this problem in response to W. T. Holser's work on the fugacity of water at high temperatures and pressures, and for his constant encouragement during the execution of this work which has been based on the *P-V-T* data of steam and of acetylene investigated by Professor R. Kiyama and his collaboraters.

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